

# Anion-exchange behavior of rutherfordium and dubnium in pure HF solution

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Many attempts have been made to study the aqueous chemistry of element 104, rutherfordium, and element 105, dubnium [1]. Differences in the complex formation among Rf, Db and their lighter homologues were deduced from some of the experiments, and some yielded conflicting results [1]. Although several experiments for Rf and Db in various HF solutions have been performed [2-5], enough data have not been accumulated to discuss in detail the fluoride complexations and/or relativistic effects. In the present work, we have investigated the chemical behavior of Rf and Db together with their group-4 and group-5 homologues by an anion-exchange chromatography in pure HF solution expected to be a fast and simple reaction mechanism to form anionic complexes.

The isotopes <sup>261</sup>Rf, <sup>85</sup>Zr, and <sup>169</sup>Hf were produced in the <sup>248</sup>Cm(<sup>18</sup>O,5n), <sup>nat</sup>Ge(<sup>18</sup>O,xn), and <sup>nat</sup>Gd(<sup>18</sup>O,xn) reactions, respectively, at the JAERI tandem accelerator [6]. On-line anion-exchange separations for Rf, Zr, and Hf in 3.9-13.9 M HF solutions were performed using the Automated Ion exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) [7]. AIDA enables us to perform cyclic discontinuous chromatographic separations in aqueous phase and automatic detections of  $\alpha$ -particles within a typical cycle time of 1 - 2 min. The reaction products recoiling out of the target were transported by the He/KCl gas-jet system to AIDA, and were dissolved with 240  $\mu$ L of 3.9 to 13.9 M HF and fed into an anion-exchange column (MCI GEL CA08Y, 1.6 mm i.d.  $\square$ ~7.0 mm) at a flow rate of 0.74 mL/min. Figure 1 shows typical elution curves of short-lived <sup>85</sup>Zr and <sup>169</sup>Hf in 14 M HF solution. These elution curves exhibit a good performance of the present anion-exchange separation system, expecting that the chemical equilibrium is established. The effluent was collected on a Ta dish as Fraction 1 and evaporated to dryness with hot He gas and a halogen heat lamp. The products remaining in the column were eluted with 210  $\mu$ L of 4.0 M HCl. This effluent was collected on another Ta dish and evaporated to dryness as Fraction 2. Each pair of Ta dishes, Fractions 1 and 2, was automatically transferred to the  $\alpha$  spectrometry station equipped with the eight 600 mm<sup>2</sup> PIPS detectors. Figure 2 shows typical  $\alpha$  particle energy spectra for Fractions 1 and 2. From the activities  $A_1$  and  $A_2$  observed in Fractions 1 and 2, respectively, the percent adsorption (%ads) on CA08Y was evaluated by the equation: %ads = 100 $A_2$ /( $A_1$  +  $A_2$ ). The %ads values of Rf, Hf and Zr in the various concentrations of HF are shown in Figure 3. This result shows a notable difference in the sorption behavior between Rf and its homologues Zr and Hf. The %ads values of Zr and Hf are in good agreement with each other and both decrease steeply with an

increase of the HF concentration above 8 M. Although the %*ads* of Rf also decreases with the HF concentration, the values are apparently smaller than those of Zr and Hf, suggesting that the fluoride complexing strength of Rf is weaker than that of Zr and Hf.

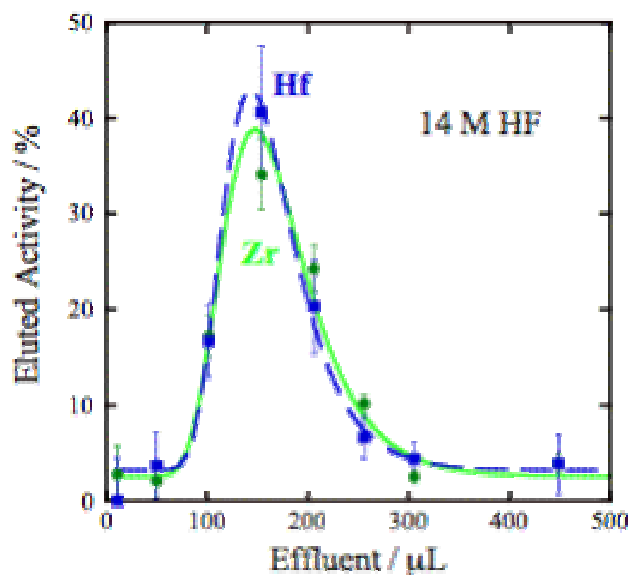


Figure 1. Elution curves for  $^{85}\text{Zr}$  and  $^{169}\text{Hf}$  in 14 M HF from an anion-exchange column (MCI GEL CA08Y, 1.6 mm i.d.  $\square \sim 7.0$  mm) at a flow rate of 0.74 mL/min.

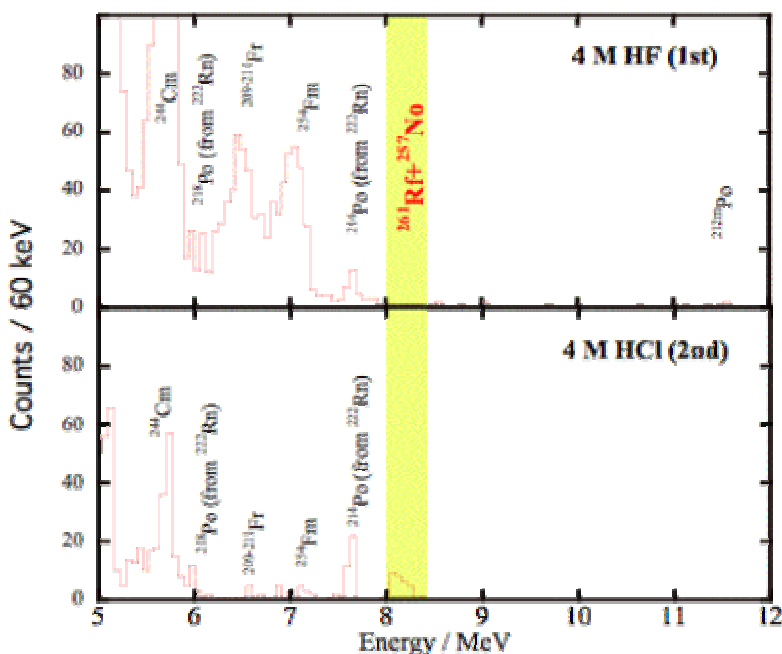


Figure 2.  $\alpha$ -particle energy spectra of two eluted fractions: (upper) 4 M HF and (lower) 4.0 M HCl.

On the other hand, we are also interested in a fluoride complexing strength of Db and its group-5 homologues, Nb and Ta, and pseudo-homologue Pa on the anion-exchange resin. The sorption sequence of  $\text{Ta} \geq \text{Nb} \gg \text{Pa}$  in 2–15 M HF solutions was observed in the batch experiment, and the %*ads* value of Db

together with Ta in a 14 M HF solution was investigated.  $^{262}\text{Db}$  and  $^{169}\text{Ta}$  were produced in the  $^{248}\text{Cm}(^{19}\text{F}, 5n)$  and  $^{147}\text{Sm}(^{19}\text{F}, xn)$  reactions, respectively, at the JAERI tandem accelerator [6]. 1702 anion-exchange separations were conducted using AIDA with a small column of 1.0 mm i.d.  $\times$  3.5 mm. It was found that the %ads value of Db is smaller than that of Ta, suggesting that the sequence of the fluoride complexing strength is  $\text{Ta} \geq \text{Nb} > \text{Db} \geq \text{Pa}$ .

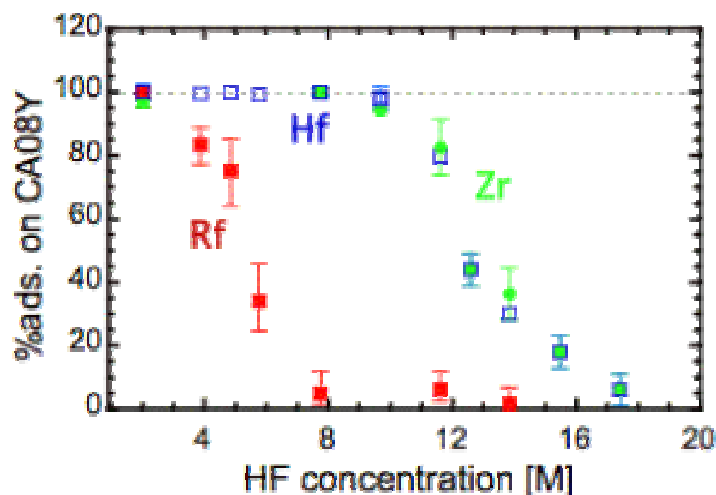


Figure 3. Variation of the percent adsorption (%ads) of Zr, Hf, and Rf on CA08Y as a function of the HF concentration.

## References

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